

Optical properties of silica colloids suspensions in electric field

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Abstract. We studied the optical properties of silica colloids suspensions made of nanospheres having an average diameter of 50, 90, 120, and 300 nm in electric field. It was illustrated that a colloidal suspension with a particle size of 120 nm shows a dramatic change of the reflection peak position in response to the applied potential. With the increase of the concentration, the position of peak maximum slightly blue-shifted and the reflection intensity slightly increased. The impact of solvents on optical properties of silica colloids suspensions was studied. It was demonstrated that the position of peak maximum has a dramatic change only in propylene carbonate; there were no marked changes in ethylene glycol and water. The intensity of reflection peak was strongest in water. We analyze the mechanism and attribute this phenomenon to the hydrogen-bonding ability of the solvents.

1. Introduction

The self-organization of colloidal building blocks has drawn the attention of researchers in the field of materials chemistry and soft condensed-matter physics [1]. Responsive photonic crystals [2] can be composed of these colloidal building blocks. They have a wide range of applications in colour displays [3, 4], bio- and chemical sensors [5], photonic printing, decoration [6] and anti-counterfeit labels [7]. In principle, one can achieve these applications by altering their periodicity and dielectric constants in response to an electrical, magnetic, or temperature [8], light, molecules and ions, applied forces. Among them, magnetic and electric fields are considered to be the optimal stimuli for modulation of the lattice constants of colloidal crystals and inverse opals for display applications. The corresponding materials include Fe_2O_3 [9], $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ [10], $\text{ZnS}@ \text{SiO}_2$ [11], highly charged polystyrene(PS) [12], SiO_2 [13], TiO_2 [14] and so on, among these various inorganic materials, silica has long been considered as an ideal candidate for generating photonic crystals due to the easiness in processing these materials as spherical colloids with truly monodisperse sizes and in copious quantities [13].

The majority of these studies, however, have been limited to solid samples made of silica spheres [4, 15], for example, Hernan Miguez [5,16] present a method to create mesostructured bragg reflectors in which the building blocks are nanoparticles of SiO_2 and TiO_2 . Arsenault et al. [3] fabricated photonic crystals comprised of a silica-metallopolymer composite to demonstrate that the lattice spacing of colloidal crystals could be modulated by electric field-assisted swelling. In addition, a type of particle array which was formed by mixing two different-sized particles shows an angle-independent colour [17]. They are all solid samples made of silica spheres. Additionally, low contrast of refractive index between silica and the solvent is another reason for the loss of attention in suspensions. Only few demonstrations involved the optical properties of silica colloids suspensions in electric field.

In this paper, we employ silica colloids suspensions consisting of different diameter of monodispersed spherical silica to research the optical properties in electric field and find that their peak position of the optical reflection spectra in the suspensions will shift with the variation of the electric field. Based on the photonic properties in electric field, we analyze the mechanism of it.

2. Experimental

2.1. Materials

Tetraethoxysilane($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$, A.R.), ethanol($\text{C}_2\text{H}_6\text{O}$, A.R.), $\text{NH}_3\cdot\text{H}_2\text{O}$ (25%, A.R.) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Propylene carbonate (99%) and ethylene glycol were purchased from Aladdin Chemicals. Indium tin oxide (ITO) coated glasses with a resistivity of $7\ \Omega\cdot\text{cm}$ was purchased from Corning Corp. All chemicals were used as received without further purification. The water used in this work was deionized (DI) water from a Millipor-Q purification system (Millipore, USA) of resistivity $18.2\ \text{M}\Omega\cdot\text{cm}$.

2.2. Synthesis procedures.

SiO_2 prepared using the ammonia-catalyzed Stöber method [13] is very uniform. This synthesis route is based on the hydrolysis of tetraethoxysilane in an alcohol–ammonia solution. We can obtain different diameter of monodispersed spherical silica particles (50 nm, 90 nm, 120 nm, 300 nm) through adjusting the proportion of ethanol, $\text{NH}_3\cdot\text{H}_2\text{O}$ and H_2O .

2.3. Preparation of devices.

The photonic display cell consists of transparent top and bottom electrodes separated by $200\ \mu\text{m}$ thick epoxy spacers. SiO_2 suspension (5.4–20v% in propylene carbonate) was injected in between those electrodes by using the conventional injection syringe, then we apply an electric field to the photonic display cell.

2.4. Characterization.

The morphology and grain size of the samples were examined by a Hitachi S4800 field emission scanning electron microscope (FESEM) and FEI Tecnai G2 F20 transmission electron microscope (TEM). The reflection spectra of these silica colloids suspensions in electric field were measured by an Ocean Optics HR 2000CG-UV-NIR spectrometer coupled with a six-around-one reflection/backscattering probe. Electric field was applied to silica colloids suspensions by a function generator (Agilent, 33220A) for DC power supply.

3. Results and discussion

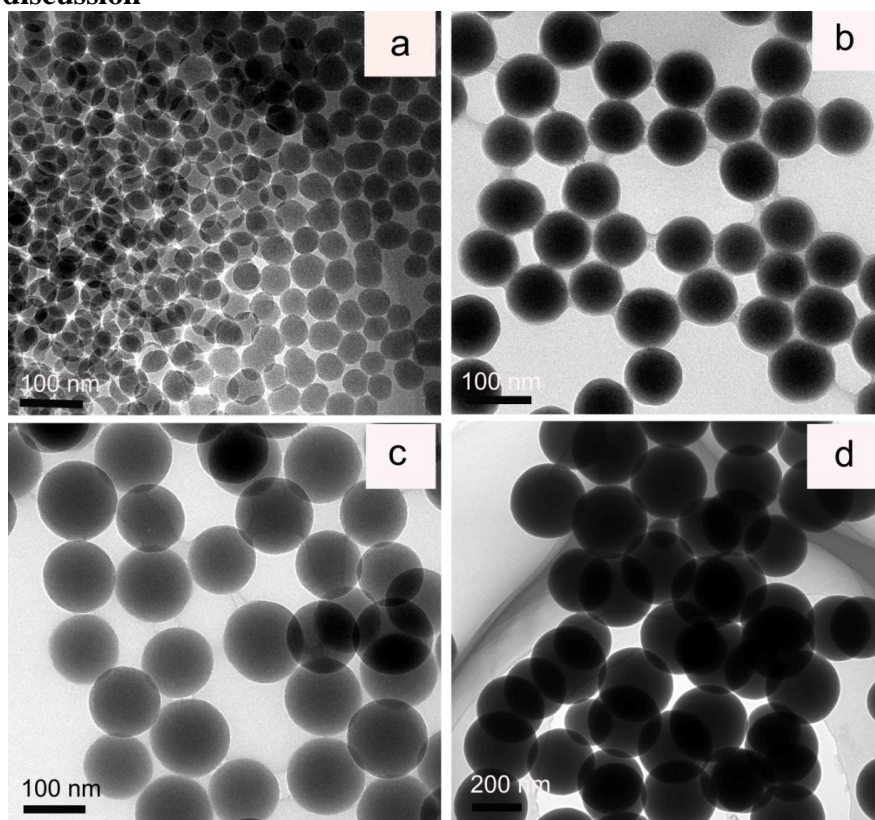


Fig.1 TEM images of monodispersed spherical silica a) 50 nm, b) 90 nm, c) 120 nm, d) 300 nm.

Fig.1 illustrates the morphologies of representative SiO₂ particles with an average diameter of 50 nm, 90 nm, 120 nm, 300 nm. The SiO₂ particles appear monodisperse.

As seen from the reflection spectra, the photonic properties altered along with the electric field. Fig.2a, 2b and 2d show the position of peak maximum have remained about the same but the reflection intensity slightly decreased in response to an increasing electric field. Fig.2c shows a dramatic change of the position of peak maximum in response to applied electric field. In the absence of the electric field, a reflection peak at 710 nm appeared due to the Bragg diffraction from the polycrystalline structures [18]. When an electric field of 0.5 v was applied, the reflection peak maximum value slightly decreased. When the electric field was enhanced to 1.0v, the position of peak maximum blue-shifted to 600 nm and another peak at about 750 nm appeared. When further enhancing the electric field to 1.5 v, the peak position at 600 nm shifted to a shorter wavelength at 525 nm and the reflection intensity slightly increased, while another peak remained at 750 nm but the reflection intensity slightly decreased.

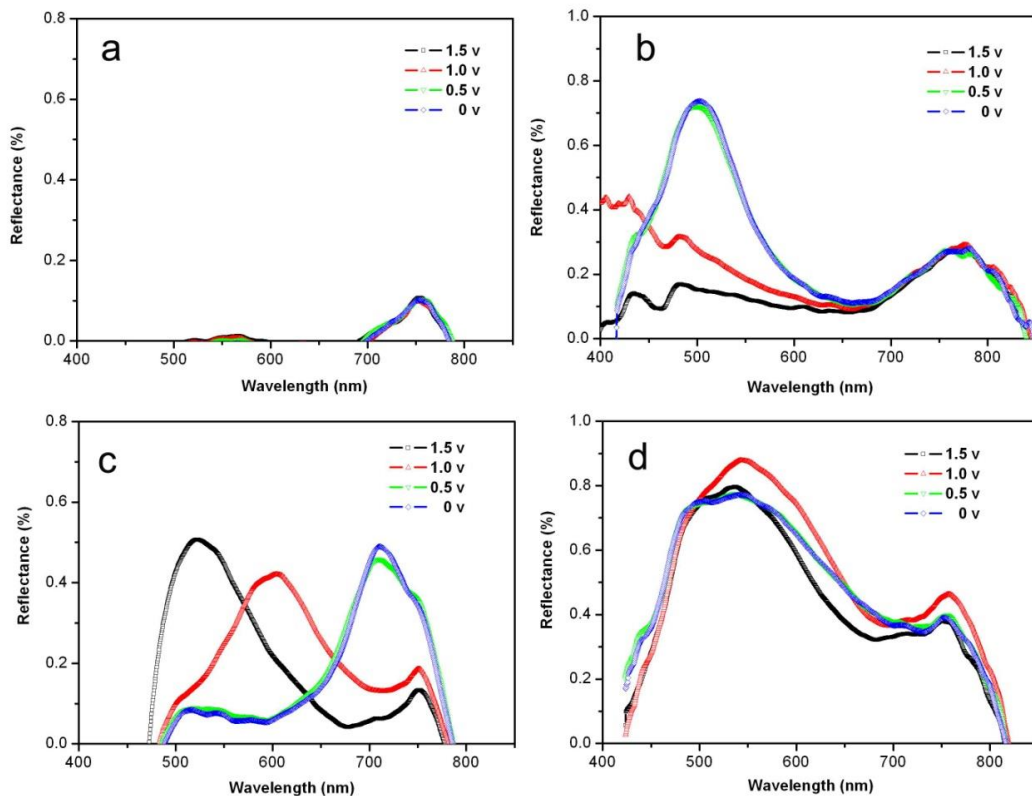


Fig.2 Reflection spectra of silica colloids suspensions at concentrations of 5.4v% in propylene carbonate with different diameter taken at increasing bias voltage. a) 50 nm, b) 90 nm, c) 120 nm, d) 300 nm.

From the description above, Fig.2a, 2b and 2d show that the reflective peak intensity is gradually changed without obvious peak position shift under external electric field, while Fig.2c shows a dramatic change of the position of peak maximum. The different response of the position of peak maximum to external electric field is due to the colloidal structures. Among the four kinds of suspensions made of SiO₂ particles with different sizes, only SiO₂ particles with an average diameter of 120 nm can assemble the colloidal structures with the average inter-particle distance on length scales comparable to visible wavelengths, so we can see a dramatic change of the position of peak maximum, which are attributed to the Bragg diffraction of visible light.

The explanation to the change of reflective peak intensity can be offered by the Fresnel equation [19], as follows:

$$R_s = \left[\frac{n_1 \cos \theta_i - n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2}}{n_1 \cos \theta_i + n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2}} \right]^2$$

Where R_s is the reflection coefficient, n_1 is the refractive indices of air, n_2 ($\phi \cdot n_{\text{spheres}} + (1-\phi) \cdot n_{\text{media}}$, ϕ :solid fraction) is the effective refractive index, and θ_i is the angle that the incident ray makes to the normal of the interface. Because the spherical SiO_2 particles are negatively charged, so the particle is approached to the positive electrode by electrostatic force under electric field and the solid fraction(ϕ) is changing in the area near the positive electrode. With the change of solid fraction (ϕ), the reflection coefficient will change as well.

The shift of reflected spectrum peak position is not only related to the diameter of particle, but also related to the concentration. We prepare SiO_2 suspensions (120 nm) with different concentrations (5.4 v%, 10.0 v%, 15.0 v%, 20.0 v%) in propylene carbonate, the suspension displays different colours in the absence of external electric field. The variation of colour is from pink to blue as the concentration increases, which is corresponding to the variation of reflection spectra.

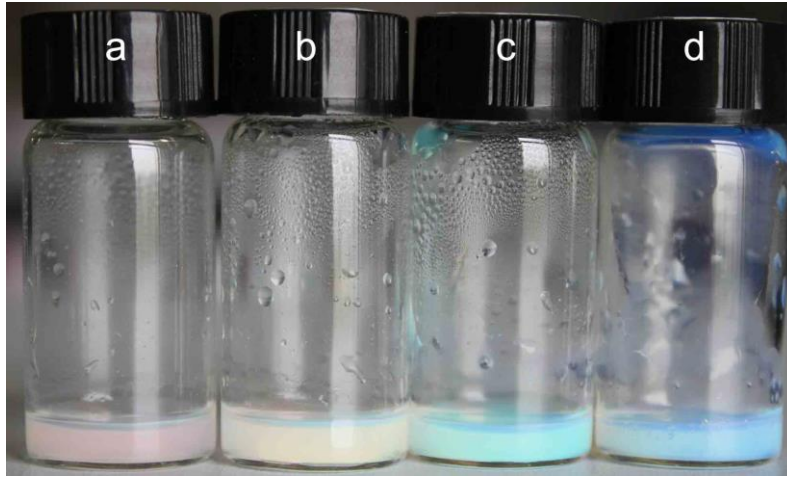


Fig.3 Photograph of SiO_2 suspensions (120 nm) with different concentrations (5.4 v%, 10.0 v%, 15.0 v%, 20.0 v%) in propylene carbonate in the absence of external electric field.

Just as demonstrated in Fig. 4a, in the absence of the electric field, a reflection peak blue-shifted to 600 nm and the intensity is higher compared with the results of Fig. 2c due to the higher concentration. As the electric field increases, the blue-shift of the reflection wavelength from 600 nm to 410 nm occurred. Fig. 4b and 4c show the reflectance spectra of the SiO_2 (120 nm) colloids suspensions at different concentrations (15.0 v%, 20.0 v%) in propylene carbonate under electric field. Compared with the results of Fig. 4a, the position of peak maximum slightly blue-shifted and the reflection intensity sharp decreased. While the electric field increases to 1.5v, the peak position remained about the same. The high concentration may offer the proper reason for this phenomenon, because the inter-particle distance has reached the limit.

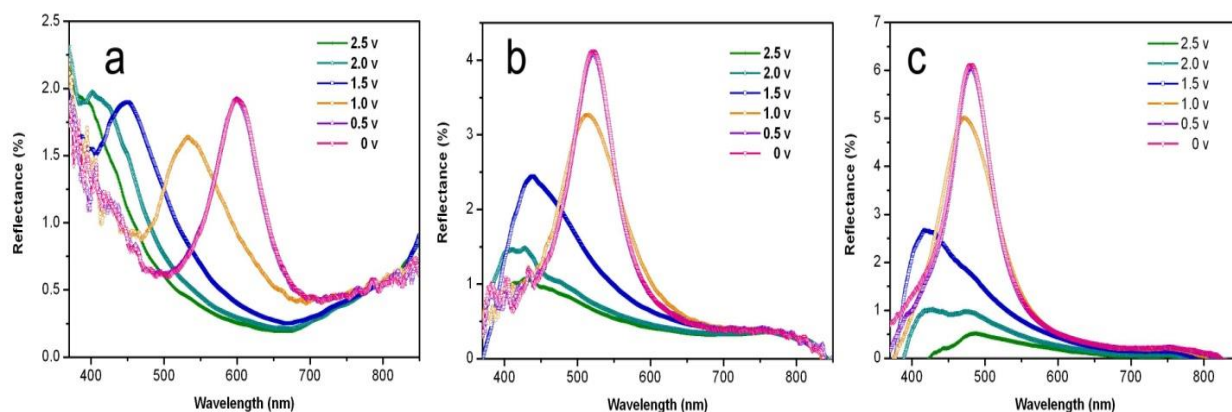


Fig.4 Reflection spectra of SiO₂ suspensions (120 nm) at different concentrations (10.0 v%, 15.0 v%, 20.0 v%) in propylene carbonate ().

It is well-known that multi-layered colloidal crystals made of colloidal particles will appear under a DC field because of the electrophoretic movement [20]. The number of periodic colloidal layers stacked on electrode surface is varied proportional to the electric field gradient, and the thickness change directly affects the intensity of reflection [21]. This theory is proved by the result as is shown in Fig.5, the SiO₂ (120 nm) nanospheres at concentrations of 5.4 v% in propylene carbonate assembles into a stratified structure in the positive electrode, while only monolayer consists of SiO₂ nanospheres stays behind on the negative electrode after applying electric field to the colloidal dispersion.

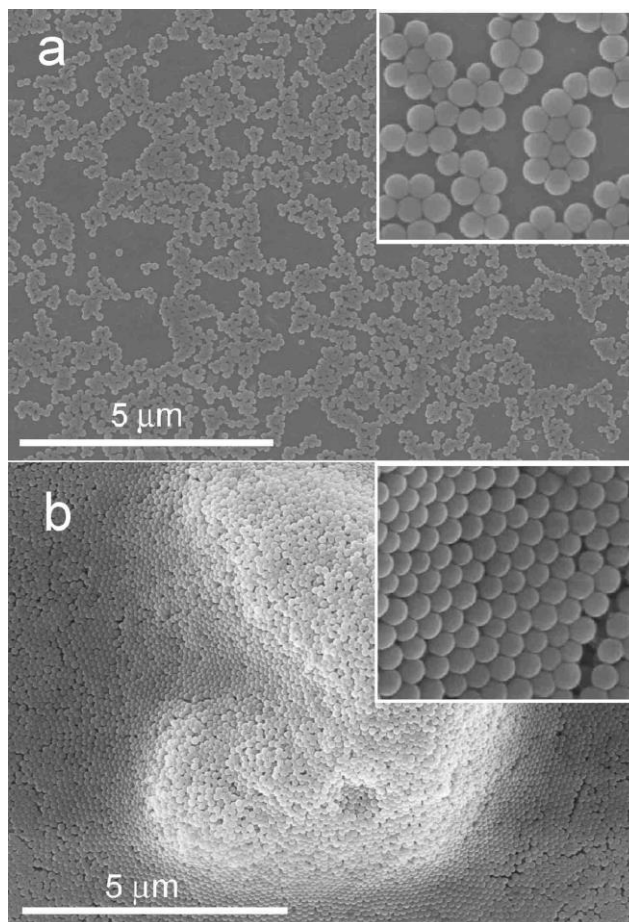


Fig.5 SEM images of the colloidal layers after drying. (a) and (b) is formed on the negative and positive electrode surface in the test cell after applying voltage respectively, the SEM image (inset) is magnification of the local region .

To examine the reversibility of the bandgap shift, we took off the electric field after applied DC field varied from 0 to 2.5 v to SiO₂ suspensions (120 nm) at concentrations of 10.0 v% in propylene carbonate. As shown in Fig. 6, the reflectance peak returned to its original position with low reflective peak intensity due to the formation of particle aggregates on electrodes after 390 s.

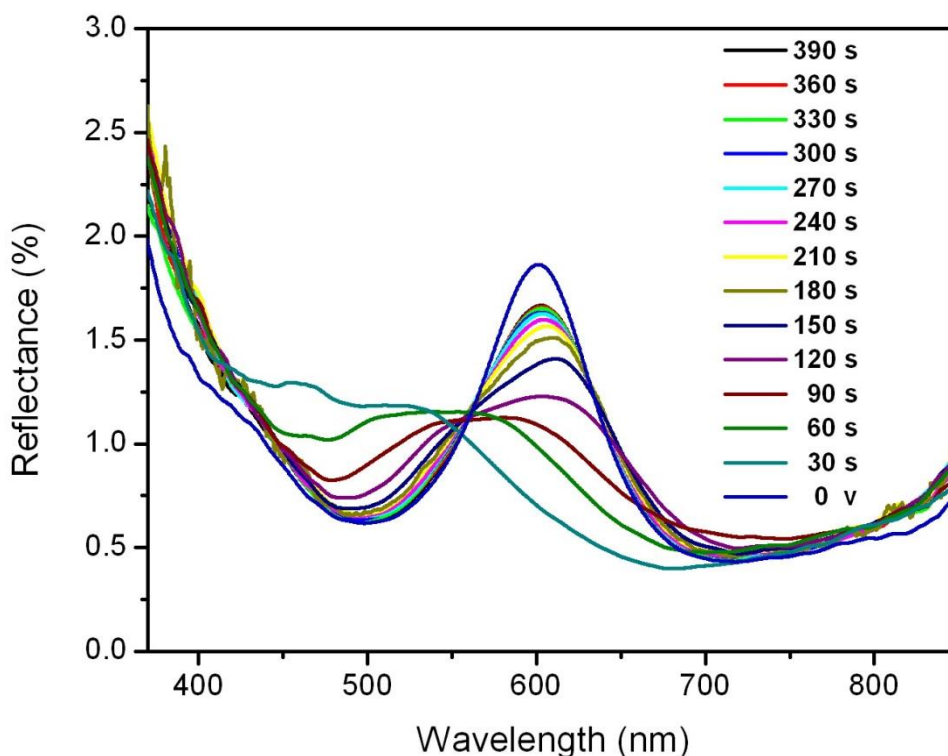


Fig.6 Time-dependent reflection spectra of SiO₂ suspensions (120 nm) at concentrations of 10.0 v% in propylene carbonate after turning off the DC power supply.

It is noted that the SiO₂ (120 nm) suspensions of ethylene glycol and H₂O, the reflective peak intensity is gradually changed without peak position shift under the external electric field. We analyze the mechanism and attribute this phenomenon to the hydrogen-bonding ability of the solvents which is a key factor in determining the nature of interparticle interactions and the resulting reflection spectra [22]. Propylene carbonate is weakly hydrogen-bonding liquid. The liquid interacts weakly with the silica surface, thus enabling adjacent particles to adhere through H-bonds between the surface silanols groups. The particle-particle bonds are weak, so there will be a dramatic change of the position of peak maximum in response to applied electric field. As to ethylene glycol and H₂O which are strongly hydrogen-bonding liquids. These liquids are able to H-bond with the silanols on the silica surface, resulting in the formation of a solvation layer around each particle. This leads to repulsive solvation forces which stabilize the silica particles so that peak position remains the same under the external electric field. For the SiO₂ (120 nm) suspensions of ethylene glycol, the reflective peak intensity is remain unchanged until the electric field was enhanced to 2.5 v, the insensitivity to the electric field may be due to the high viscosity of ethylene glycol that restricts the movement of SiO₂ (120 nm) nanospheres. For the SiO₂ (120 nm) suspensions of H₂O, the reflective peak intensity is very high, this may because of the high dielectric constant.

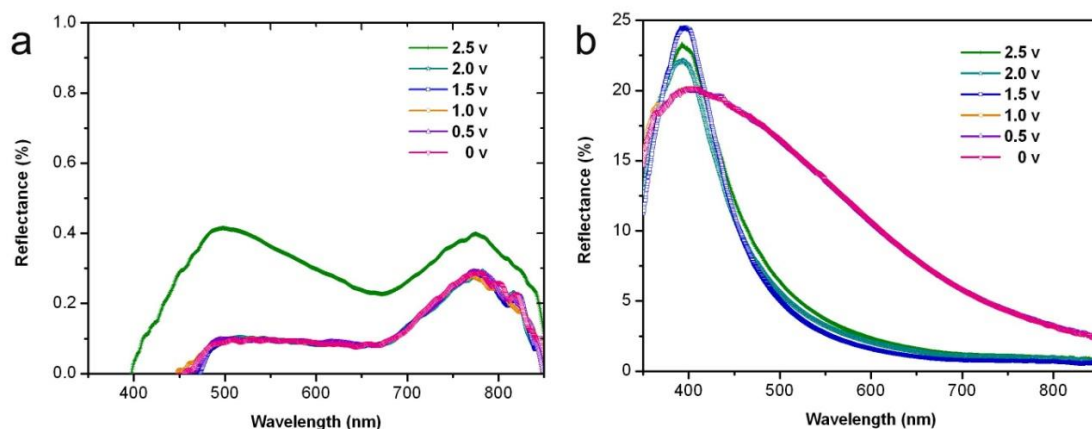


Fig.7 Reflection spectra of SiO₂ suspensions (120 nm) at concentrations of 5.4v% in a) ethylene glycol, b) H₂O

4. Conclusions

In summary, we have investigated in detail the spectroscopic properties of different diameter of SiO₂ nanoparticle suspensions under external electric field. The SiO₂ (120 nm) suspensions show a dramatic change of the reflection peak position in response to applied potential. With the increase of the concentration, the position of peak maximum slightly blue-shifted, while the electric field increases to 1.5 v, the peak position remained about the same. The solvent-dependent reflection of suspensions under external electric field was carried out by dispersing the colloidal nanospheres in solvents, including propylene carbonate, ethylene glycol and water. It is shown that the position of peak maximum has a dramatic change only in propylene carbonate. We anticipate that our results provide useful information for understanding the photonic properties of silica colloids suspensions in electric field and an important platform for sampling the aggregation and assembly at the single-particle level.

Acknowledgments

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